ship is obtained. Data for the branched chain isomers, however, indicate that the relative yields of hydrogen and methane are not proportional to the fractional concentration of C–H and C–CH_3 bonds in the bombarded molecule. This selective decomposition of organic compounds by ionizing radiation has been recently discussed[5] in terms of competing free radical and rearrangement processes.

To obtain information on the effect of isomerism on the radiation chemistry of organic acids, we have studied the decomposition of several series of isomeric acids in the ozonizer discharge which has been shown[6] to produce chemical change by processes similar to those obtained with high-energy radiation. A previous paper[7] reported the decomposition of the toluic acids. The present paper reports a similar study of the valeric acid isomers. Gaseous decomposition products obtained from the valeric acids in the liquid state at 0° are shown in Table I. By comparing the CH_4/H_2 yield ratios for the four isomeric acids, it is seen that the relative yield of methane to hydrogen is not proportional to the C–CH_3/C–H bond ratio in the bombarded molecule. In fact, the methane to hydrogen yield ratio for trimethylacetic acid is actually smaller than the corresponding values observed with the other three compounds. The yield of methane relative to carbon dioxide plus carbon dioxide plus carbon monoxide also shows a minimum value with the tertiary acid. Increasing substitution on the alpha carbon atom results in a decrease in the probability of methane formation with a corresponding increase in the relative yield of higher hydrocarbons. A quantitative analysis of the higher hydrocarbon fraction was not undertaken; qualitative fractionation, however, indicated the presence of ethane and hydrocarbons with higher boiling points. A more detailed discussion of these reactions will be presented in a later paper.

TABLE I

GASEOUS PRODUCTS FROM THE VALERIC ACIDS IN THE OZONIZER DISCHARGE (VOLUME %)

	n-Valeric		Isovaleric		Methyl-ethyl-acetic		Tri-methyl-acetic	
H_2O	11.5	11.3	10.7	11.2	9.3	8.3	14.5	14.8
CO_2	10.0	10.0	10.7	9.8	10.2	10.7	18.3	19.3
CO	16.6	15.3	22.0	22.4	26.8	25.5	22.6	22.6
H_2	54.3	54.6	40.7	40.6	38.0	40.1	17.7	17.1
CH_4	8.8	9.0	8.2	8.4	8.3	7.8	1.8	0.5
Other[a] hydrocarbons	0.2	0.2	7.3	7.0	6.8	7.0	26.3	25.0

[a] Condensable in liquid air after removing water and carbon dioxide.

Experimental

Isovaleric acid (b. p. 176–176.5°) and methylethylacetic acid (b. p. 173–174°), obtained from Eastman Kodak Co., were used without further purification. *n*-Valeric acid (b. p. 186.2°) was prepared by hydrolysis of *n*-valeronitrile and purified by fractional distillation. Trimethylacetic acid (b. p. 173–174°) was prepared by the method of Puntambeker and Zoellner.[8]

The all-glass discharge chamber,[9] the temperature of which was controlled by an ice-water-bath, was connected through stopcocks to a manifold, to a product gas storage bulb, and to a Toepler pump which was used to transfer the decomposition products to a gas microanalyzer.[10] The entire system could be evacuated to 10^{-5} mm. by a mercury diffusion pump attached to the manifold through a liquid-air trap. The transformer and experimental procedure were identical with those previously described.[8]

---

[5] M. Burton, *J. Phys. Chem.*, **51**, 786 (1947).

[6] G. Glockler and S. C. Lind, "The Electrochemistry of Gases and Other Dielectrics," John Wiley and Sons, Inc., New York, N. Y., 1939.

[7] C. N. Stover and W. M. Garrison, THIS JOURNAL, **72**, 2793 (1950).

[8] "Organic Syntheses," 2nd ed., Vol. I, John Wiley and Sons, Inc., New York, 1944, p. 524.

[9] E. Warburg, *Z. tech. Physik*, **4**, 450 (1923).

[10] C. N. Stover, W. S. Partridge and W. M. Garrison, *Anal. Chem.*, **21**, 1013 (1949).

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF WYOMING
LARAMIE, WYOMING

RECEIVED MARCH 17, 1950

Polymorphism of 17-Ethinylestradiol

BY RICHARD PHEASANT

17-Ethinylestradiol has been described with a melting point of 146°.[1] A second polymorphic form, m. p. 183° cor., has been encountered and conditions have been found which effect the interconversion of the two forms.

Samples of pharmaceutical grade ethinylestradiol which melted in the normal manner at 146° were sometimes observed to be slightly cloudy in appearance. Sustained heating at 150 to 160° caused these samples to resolidify completely to acicular crystals. This crystalline form underwent no physical change on cooling. The melting point of this form was about 183°, at which temperature it melted completely to a clear liquid, which did not crystallize on cooling but formed a glassy mass. However, it could be made to crystallize as either the 146 or the 183° melting form by seeding with the desired form. Seeding with a mixture of both forms, even at a temperature below 140°, produced only the higher melting form.

A methanol solution prepared from the high-melting form gave the low-melting form upon concentration and cooling. The mother liquor was diluted with ether and upon standing for several days gave crystals of the high-melting form.

A sample of the 183° melting form gave the following analysis: Calcd. for $C_{20}H_{24}O_2$: C, 81.04; H, 8.16. Found: C, 80.80; H, 8.30. Infrared absorption spectra were determined on samples of both forms, both in chloroform solution and in mineral oil suspension.[2] The chloroform solutions gave identical absorption curves between 2 and 12 microns. Curves from the mineral oil

---

[1] Inhoffen, Logemann, Hohlweg and Serini, *Ber.*, **71**, 1024 (1938).

[2] The author is indebted to W. B. Tarpley, Research Laboratories of this company, for the absorption spectra.

suspensions were dissimilar only in the region from 8 to 12 microns, possibly due to the differences in crystal structure.

Biological assays of the two forms showed no significant difference in estrogenic activity.[3]

(3) Modified Kahnt–Doisy method, by S. Margolin and M. T. Spoerlein, Biological Laboratories of this Company.

QUALITY CONTROL DEPARTMENT
SCHERING CORPORATION
BLOOMFIELD, N. J.

RECEIVED MAY 9, 1950

Isomerization of Saturated Hydrocarbons. VIII.[1] The Effect of Oxygen and Light upon the Isomerization of Methylcyclopentane in the Presence of Aluminum Bromide

BY HERMAN PINES, EUGENE ARISTOFF[2] AND V. N. IPATIEFF

The promoting effect of oxygen upon the isomerization of *n*-butane and *n*-pentane in the presence of either aluminum chloride or aluminum bromide has been reported previously.[3] This study has now been extended to determine whether oxygen in the presence of aluminum bromide but in the absence of added hydrogen bromide promotes the isomerization of saturated cyclic hydrocarbons such as methylcyclopentane to cyclohexane. The experiments were conducted in either quartz or Pyrex reaction tubes.

It was noticed that in diffused light, and a Pyrex reaction tube, with methylcyclopentane, aluminum bromide and oxygen in a molal ratio of 100:2:0.2, isomerization of methylcyclopentane to cyclohexane does not occur. When the reaction tube was exposed for eighteen hours to a quartz cadmium–mercury arc lamp 6% of the methylcyclopentane was isomerized; the extent of isomerization was increased to 13% when a quartz reaction tube instead of a Pyrex one was used.

The introduction of a larger amount of oxygen into a Pyrex reaction zone, namely, 1 mole equivalent of oxygen per 100 moles of methylcyclopentane and 4 moles of aluminum bromide, caused the isomerization of 15% of methylcyclopentane; when a quartz reaction tube was used and irradiated, 42% of cyclohexane was formed.

In line with previous observations[1,4,5] it was noticed that the presence of about 0.04 mole per cent. of benzene in methylcyclopentane greatly reduces the degree of isomerization. The experimental results are summarized in Table I.

During the course of this study it was observed that aluminum bromide *per se* placed in a quartz tube and irradiated did not change coloration. It was noticed however that when aluminum bromide in the presence of oxygen was irradiated for 0.5–1 hour the tube was filled with brown vapors, which became more deeply colored as the time of irradiation increased. The mechanism by which the oxidation of aluminum bromide proceeds was not studied. It is very likely that the promoting effect of the oxygen is due to the oxidation of aluminum bromide with formation of bromine. The latter then reacts with methylcyclopentane to form bromomethylcyclopentane, which is a chain initiator for the isomerization.[6] The oxidation of aluminum bromide in solution in hydrocarbons seems to proceed even in diffused light.

The inhibiting effect of benzene upon the isomerization of methylcyclopentane is not entirely unexpected; it is most likely due to the removal of the chain initiator through the reaction with benzene, as has been shown previously.[1,5]

TABLE I

ISOMERIZATION OF METHYLCYCLOPENTANE

Expt.	Irradiation, hours	Reaction tube[b]	Methylcyclopentane used, moles $\times 10^2$	Reactant charged moles per 100 moles of methylcyclopentane			Cyclohexane produced, %
				$AlBr_3$	O_2	C_6H_6	
1	18[a]	P	2.22	2.01	0.18	0	0
2	18[a]	P	3.10	4.00	1.05	0	15
3	18	P	2.11	2.02	0.18	0	6
4	18	Q	1.37	1.99	.17	0	13
5	18	Q	1.04	4.02	.96	0	42
6	18	Q	2.60	2.04	.20	0.037	0
7	18	Q	1.00	3.98	.96	0.039	6

[a] In experiments 1 and 2 the reaction tubes were not irradiated. [b] P, Pyrex reaction tube; Q, quartz reaction tube.

Experimental

The high vacuum apparatus and procedure have been described previously.[1,6] Linde oxygen was introduced into the apparatus through a phosphorus pentoxide drying tube. After being measured in the calibrated portion of the Töpler pump, the oxygen was transferred to an ampoule having a thin walled break-off. The sealed ampoule was carefully placed in the reaction tube, then the latter evacuated. After the other reactants had been added, the reaction tube was sealed off then shaken, in order to break the thin bulb of the ampoule containing oxygen. The composition of the hydrocarbons obtained from the reaction was determined by means of infrared absorption spectra.

---

[1] For paper VII of this series see H. Pines, E. Aristoff and V. N. Ipatieff, THIS JOURNAL, **72**, 4055 (1950).

[2] Universal Oil Products Company Predoctoral Research Fellow 1947–1949.

[3] H. Pines and R. C. Wackher, THIS JOURNAL, **68**, 599 (1946).

[4] J. M. Mavity, H. Pines, R. C. Wackher and J. A. Brooks, *Ind. Eng. Chem.*, **40**, 2374 (1948).

[5] H. Pines, E. Aristoff and V. N. Ipatieff, THIS JOURNAL, **71**, 749 (1949).

[6] H. Pines, B. M. Abraham and V. N. Ipatieff, *ibid.*, **70**, 1742 (1948).

THE IPATIEFF HIGH PRESSURE AND
CATALYTIC LABORATORY
DEPARTMENT OF CHEMISTRY
NORTHWESTERN UNIVERSITY
EVANSTON, ILLINOIS

RECEIVED MARCH 22, 1950

The Structure of Methyl Acetylacrylate[1]

BY SAMUEL RAYMOND

Methyl acetylacrylate was first prepared in 1914 by Pauly, Gilmour and Will[1a] by the dehydro-

---

[1] This work was supported by a grant from the National Institutes of Health and from the John and Mary R. Markle Foundation.

[1a] Pauly, Gilmour and Will, *Ann.*, **408**, 119 (1914).